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The Effect of the Addition of Various Elements to Cast Iron

Part I

One of a Series of Papers on Cast Iron and Its Manufacture

BY ***Dr. Edward E. Marbaker,***
Director of Foundry Research,
Whiting Corporation

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The Effect of the Addition of Various Elements to Cast Iron

A Review of the Literature

PART I

By *Edward E. Marbaker, Ph.D.*[1]

INTRODUCTION

CAST iron, as we know, is a very complex alloy of iron with several elements, the chief one of which is carbon. Generally speaking, cast iron and steel are both included in the classification iron-carbon alloys, but there are vast differences between them. Roughly, when less than 2% carbon is present, the alloy is called a steel and above 2% it is called cast iron. Actually steels seldom contain as much as 2% carbon and cast iron as little as that amount. Another difference between the two alloys is that steel contains little or no graphitic carbon, all the carbon existing in some combined form, the strongest steel containing 0.90% combined carbon and having a structure known as "pearlitic" by metallurgists. Cast iron, on the other hand, consists of free carbon, in the form of flakes or nodules of graphite embedded in a metallic matrix, which may be more or less pearlitic in structure. As in the case of steels, it has been proved with cast iron that the more pearlitic the structure of the ground mass, the stronger the iron, and this relation is further improved when the graphite particles are reduced to the smallest possible size, and are uniformly distributed.

Cast iron does not consist of iron and carbon alone, but ordinarily there are present also silicon, manganese, phosphorus and sulphur. The effects of these four elements in the primary alloy of iron and carbon are very marked, and during the last twenty-five or thirty years they have been studied most carefully by metallurgists. The results of their investigations have been set forth in numerous constitutional diagrams which show how the various alloys behave at different temperatures.

Silicon is the most important of these elements because it has the property of accelerating the decomposition of iron carbide or cementite which is the constituent found when molten cast iron is allowed to solidify rapidly. Thus when low silicon irons are cast, the fracture is white because there is little fine graphite present and when the silicon is high the fracture is gray because of the considerable amounts of graphite precipitated. In the first case, the iron is very hard and cannot be machined. In the second, while it is soft and can be machined readily, it is relatively low in strength. In the attempt to balance the advantages and disadvantages of silicon, an enormous amount of metallurgical research has been carried on. Up to 3% silicon acts favorably as a softener but above that point where it ceases to influence the graphite separation, its influence is distinctly harmful[2]

Manganese is always present in cast iron in greater or lesser amounts. Like silicon it is a natural impurity, originating in the ore from which the metal was originally reduced in the blast furnace. The effect of this element, too, has been studied extensively and there is still some controversy among metallurgists as to its real value. Keep concluded that it had little influence, while other investigations have shown that the strength and hardness increase with increasing percentages of manganese. In small amounts it has no apparent effect on the combined carbon, but in high percentages it can prevent the silicon from reacting with cementite. The shrinkage increases with the manganese content. The effect of manganese is modified by the silicon present and the study of such an alloy-iron-carbon-silicon-manganese (a quarternary system, so called) becomes very complex and only a relatively small number of the possible combinations can be studied. Manganese also acts as a desulphurizer and a deoxidizer, two properties which impress the foundryman more perhaps than its metallurgical effect. The problem has now become exceedingly difficult from a metallurgical standpoint, and there are still phosphorus and sulphur to be considered. These elements also occur in the alloy naturally, having originated in the ore. Sulphur also enters the iron from the coke with which it is reduced in the blast furnace or melted in the cupola. Phosphorus forms with iron a phosphide (Fe_3P) called steadite, which is very hard. As cast iron cools, this forms a eutectic with iron carbide. The melting point of this substance is relatively low, however, and it induces in the molten iron an increased fluidity, which is of great advantage when thin sections are to be poured. Phosphorus causes decomposition of cementite but in a lesser degree than silicon, and it increases the brittleness. Up to 1% it has been found to have little effect on strength and hardness.

The effect of sulphur has been debated for years. Most foundrymen believe it to have a hardening effect and try to eliminate it as far as possible. Many processes have been devised for desulphurizing iron and the metal so treated is said to have the properties commonly attributed to high-test cast iron. Sulphur occurs in the iron as iron sulphide (FeS) and this reacts with some of the manganese present to form MnS, which is insoluble in the iron and passes out in the slag. Thus, manganese acts in a twofold manner in cast iron.

The elements which naturally accompany cast iron in

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[1] Director of Foundry Research Division, Whiting Corporation, Pittsburgh, Pa.

[2] Geiger, Handbuch der Eisen und Stahl Giesserei. Berlin: Springer, II Edition 1925, P. 83.

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called atomic weights. Hydrogen is the lightest element known, and hence its atomic weight is arbitrarily taken as one, and the atomic weight of any other element indicates how many times heavier than hydrogen it is. Thus the atomic weight can be expressed in any unit desired, the relationship always remaining the same.

In the course of the centuries ninety-two elements have been discovered and their atomic weights are known. In the foundry we are accustomed to speak of carbon, silicon, manganese, sulphur and phosphorus, all of which are elements associated with the element iron. The atomic weight of carbon is 12, of silicon 28, of manganese 55, of sulphur 32, and of phosphorus 31. These weights are used in making chemical and metallurgical calculations.

It was early recognized that certain relationships exist among the elements. The gas chlorine, the liquid bromine, and the solid iodine are very corrosive, have strong, penetrating odors, and with other elements form compounds which have similar properties. Copper, silver and gold likewise have many physical and chemical properties in common. When all the elements are studied carefully, it is found that they all fall into certain groups. When the elements are set down in the order of increasing atomic weights, it is found that every seventh element shows some similarity of properties. The characteristic property is the same but different in degree, thus copper is lighter than silver, and silver than gold. Chlorine is more corrosive than bromine, and bromine than iodine. Thus a certain property is repeated periodically.

In this way it is possible to construct the table on pages 4 and 5 in which the similar elements are found to arrange themselves in seven vertical columns. An eighth column is necessary for hydrogen and the rare gases of the atmosphere of which no compounds are known. This is known as the Periodic System of the Elements, and sets forth the law that the properties of the elements are periodic functions of their atomic weights.

Before all the elements were discovered, and incidentally at least two are still missing, the table had some blank spaces. From a study of the properties of the elements surrounding the blank, properties of the missing elements were predicted and when they were discovered, the observed properties approximated the prediction very closely. This shows that the table gives a true picture of the orderly arrangement of Nature.

It is from this point of view that it is desired to study the problem of alloy cast iron, beginning first with a presentation of the known facts, and second, to attempt to predict what elements may be expected to impart valuable properties to cast iron. It will be seen that the use of certain of the elements is not practicable. For various reasons, many of the elements have already been studied, but there are others which, by analogy, may prove to be very valuable as alloy additions to cast iron.

A study of the Periodic System of the elements gives some inkling of which elements may be valuable in alloying cast iron. The gaseous elements can be eliminated from this consideration, although it has been claimed that the presence of oxygen in small amounts increases strength and chill.[1] Also nitrogen has the property of forming metallic nitrides which bring about hardening and resistance to corrosion. However, the foundryman usually has enough trouble with gases to make him look with jaundiced eye at any proposal to consider them as alloying elements.

Among the metals of Group I of the Periodic System are to be found copper, silver, and gold. The last two can be rejected because of high cost. The effect of copper has been investigated and will be discussed later.

Group II includes beryllium, magnesium, calcium, zinc, strontium, barium, and mercury. Calcium, strontium and barium, are much alike chemically, so that if any of these were selected for study, it would be calcium because it is most plentiful and cheapest. Magnesium has been used, but as a deoxidizer. It seems to have no affinity for the iron. Beryllium is relatively a new element; that is, commercially feasible methods for its production have only recently been worked out. Very remarkable results are being obtained from alloys of beryllium with the lighter metals such as aluminum, but little has been done with it in relation to cast iron. There seems to be no record of any investigation of the influence of zinc.

In Group III, we have boron and aluminum as possibilities. The other elements in this group are known as the rare earths and are obtainable only in small quantities and with great difficulty. Thallium belongs in this group, and it is relatively easy to obtain, but nothing seems to have been done with it.

In Group IV, the all important elements carbon and silicon appear, accompanied by titanium, zirconium, cerium, thorium, tin, and lead. The last three of these apparently have not been given any consideration as alloying materials with iron, but they have, of course, been studied extensively in other directions. Titanium, zirconium, and cerium appear to act chiefly as deoxidizers.

Group V includes nitrogen, phosphorus, vanadium, arsenic, columbium, tantalum, antimony, and bismuth. Columbium and tantalum are known in metallic form and are being produced commercially, but they are very expensive, and if they were used they would act as powerful deoxidizers, and perhaps be no more valuable than aluminum or titanium. Antimony and bismuth are very valuable alloys with other metals, but apparently they have not been tried with iron. Vanadium and arsenic have been studied, the former quite extensively.

In Group VI are oxygen, sulphur, chromium, selenium, molybdenum, tellurium, tungsten, and uranium. Oxygen and sulphur have naturally received much attention. Selenium and tellurium are relatively rare and by analogy would act much like sulphur. Chromium has been studied extensively and especially in combination with nickel has given rise to some very valuable alloys of iron. Molybdenum, tungsten, and uranium have been studied and their effects are known.

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[1] J. E. Johnson, Jr., Bulletin of American Institute Mining Engineers, *85*, 1-40 (1914).

In Group VII, the only metallic element is manganese, and its importance in relation to cast iron has already been discussed briefly.

In Group VIII appears iron itself with nickel, cobalt and the platinum metals. The latter can be dismissed because of their high cost. Nickel has been studied very extensively and cobalt, its congener, has received some attention. Up to this time, nickel has proved to be the most important of all the elements used in alloying iron. The work on nickel and chromium has been so extensive that in this paper it will not be considered in detail.

The influence of the individual alloying elements will be treated in the subsequent bulletin, entitled "The Effect of the Addition of Various Elements to Cast Iron, Part II."

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The Effect of the Addition of Various Elements to Cast Iron

A Review of the Literature

PART II, The Influence of the Individual Alloying Elements

By Edward E. Marbaker, Ph.D.[1]

THE ELEMENTS OF GROUP I

COPPER. Copper is often present in pig iron in small quantities, probably not large enough to have any noticeable influence on the properties. It has been found to have certain advantages when used as an alloying element in steel, and one would naturally consider the possibility of improving the properties of cast iron by its addition. The subject has been investigated in considerable detail.

In a recent paper by Pfannenschmidt[2] the subject is reviewed and the results of the author's own experiments are given. It is stated that in 1822 a patent was granted covering the addition of 1% or less to cast iron in order to increase its resistance to corrosion by mine waters. In 1873, a British patent was granted in which it was claimed that the addition of an alloy of copper, tin, zinc, manganese, and antimony in the proportion of ¼ to ½ lb. to 100 lbs. resulted in "removing the oxides, sulphur, and phosphorus, and reducing the carbon."[3]

Beginning about 1900, the subject was studied metallurgically by Lipin[4], Smalley[5], Mikailof[6], Rolfe[7], Hotari[8], Denecke[9], and Kotzecke and Piwowarsky.[10] The results of these investigations agree quite well considering the differences in the composition of the base irons used. They may be summed up by stating that with moderate silicon contents, copper up to about 5% increases the tensile strength slightly, increases the hardness but not the brittleness, and has no effect on the structure. The resistance to corrosion by dilute acids is increased.

THE ELEMENTS OF GROUP II

BERYLLIUM. The commercial processes for the manufacture of beryllium are under the control of Siemens-Konzern, and recently under their auspices Kroll published a paper on the alloys of beryllium with iron.[11] Also Wever[12] worked out the phrase diagrams of the iron-beryllium system and compared it with the iron-carbon system, finding that the action of beryllium reduces the range of gamma iron. Illig[13] states that beryllium increases hardness and resistance to corrosion.

Apparently no specific experimental work has been carried on with reference to the effect of beryllium on cast iron, but it seems evident that this element which so profoundly affects the properties of the lighter metals, should be worthy of consideration.

CALCIUM. No record of this element having been added to cast iron as an alloying material has been found. In the form of calcium silicide it is added to molten cast iron to refine the graphite and to make possible a pearlitic structure on cooling. There is no evidence that the calcium enters the iron itself, but its value lies in the chemical action with gas or other inclusions in the metal.

Magnesium, zinc, strontium, and barium enter into alloying relations with cast iron. These elements all have a great affinity for oxygen and sulphur, and the greater part of the addition would be carried away in the slag in the form of oxides or sulphides. Mercury, of course, being a liquid, and very volatile could not be introduced into molten iron.

Moldenke[14] states that magnesium alloys perfectly with iron, and that the resulting melt is extremely fluid. Cast into iron molds the crystallization of the white fractured alloy was highly characteristic. To be used successfully in the foundry, a rich magnesium alloy must first be made, and this added to the molten iron, in order to prevent explosions. The remarkable affinity of magnesium for oxygen may make the metal very valuable in cast iron practice.

THE ELEMENTS OF GROUP III

BORON. Chemically boron is similar to silicon, but little work seems to have been done with it as an alloying element for cast iron. Wever[15] states that it acts in iron alloys like beryllium.

ALUMINUM. Within recent years aluminum has been commonly used as a deoxidizer for iron and steel, but in the foundry it has been generally believed that aluminum added in more than the small quantities necessary for this purpose renders the metal sluggish in pouring, and hard and brittle when cold. In brief, it has been held that aluminum has a deleterious effect on the metal, and this idea taken in conjunction with the somewhat unsatisfactory results of early researches on the influence of aluminum in cast iron, has caused further investigation of this subject to be neglected and consequently little fundamental research in this field has been published since 1900.[1]

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[1] Director of Foundry Research Division, Whiting Corporation, Pittsburgh, Pa.

[2] Pfannenschmidt, Die Giesserei *16*, 179-82 (1929)

[3] Journal of the Iron and Steel Institute. *8*, 229 (1874)

[4] Lipin, Stahl und Eisen *20*, I, 536-541 (1900)

[5] Smalley, Foundry Trade Journal, *26*, 519-23 (1922): 27, 3-6 (1923)

[6] Mikailof, Chimie et Industrie *18*, 453 (1927)

[7] Rolfe, Journal of the Iron and Steel Institute *205* (1928)

[8] Hotari, Bulletin College Engineering Kyushu Imperial University, 3, 169-80

[9] Denecke, Die Giesserei *15*, 307 (1928)

[10] Piwowarsky, Archiv Eisenhüttenwesen, *2*, 333 (1928)

[11] Wissenschaftlichen. Veröffentlichen aus d. Siemens Konzern, 8, 202-35 (1929)

[12] Wever, Zeitschrift für Technische Physik. *4*, 137-8 (1929)

[13] Illig, Zeitschrift angewandte Chemie. *40*, 1160-3 (1927)

[14] Moldenke. Principles of Iron Founding. New York: McGraw-Hill, (1917) P. 66

[15] Wever, Zeitschrift für Technische Physik. 137-8 (1929)

Keep[2], in 1888 and 1889, studied the affect of aluminum on white and gray cast iron using a ferro-aluminum containing 11% aluminum and 3.86% silicon. While his results are probably not conclusive, he found that 0.1% aluminum rendered cast iron sound, probably due to its influence as a deoxidizer. A precipitation of graphite in the iron was caused by the addition of 1% aluminum, with a consequent lessening of shrinkage and chill. He also found that in absence of silicon, aluminum acts more powerfully than silicon as a precipitant of graphite, with a lowering of the combined carbon content of the metal. Moldenke[3] confirmed these results in 1891 and found that a rather weak but machineable gray iron could be made from malleable iron containing 0.45% silicon, by adding 2-3% aluminum.

Hogg[4] verified Keep's results but found that when 12% aluminum is added, the carbon is all combined again. He found that the metal contained slag and the test pieces were porous.

Styffe[5] suggested the addition of 0.25% aluminum to white iron to convert a portion of the combined carbon to graphite, giving denser, more uniform and more machineable castings. He stated also that malleable iron is made harder and stronger by the addition of up to 0.75% aluminum. Above 5% all the alloys were brittle.

Melland and Waldron[6] attained similar results as to graphitization and found in the presence of low silicon there is an increase in the transverse strength and shock resisting properties, but considerable decrease in hardness and compression strength.

Adamson[7] noted that aluminum, in small quantities, reduces the depth of chill.

Everest[8] reports that with pure white iron, small additions of aluminum act like silicon in rendering the iron gray, but that its action is not so marked. Additions of aluminum above 5% introduce a hard, brittle phase into the metal, which becomes predominant at about 15%, the first graphitic range terminating at about 8%. Additions of aluminum between 20 and 26% produce iron in the second graphitic range, having limited machineability. Later Everest presents the results of adding aluminum to low silicon irons. It was found that the best properties were shown by irons containing 3-4% aluminum. With 3.70% aluminum and 1.26% combined carbon the transverse modulus of rupture was 74,592 lbs. per square inch, the tensile strength was 24,100 lbs. per square inch and a Brinell hardness of 222. Further tests indicated that aluminum irons like high silicon irons are unstable on heating and consequently would be unsuitable for use under high temperatures.

It may be of interest to note that Irmann[9] proved that liquid aluminum dissolves iron, the amount increasing as the temperature rises and decreasing as the carbon and silicon contents of the iron increase. Piwowarsky[10] was able to confirm the foregoing result with a high carbon, low silicon iron containing up to 0.1% aluminum.

THE ELEMENTS OF GROUP IV

CARBON AND SILICON. These elements are essential constituents of cast iron and should hardly be considered in any discussion of alloy additions. The content of these elements in any cast iron is the factor which to the greatest extent controls the physical properties of the alloy. It is well known that the tendency of the present day is toward a lowering of the carbon content to between 2.75 and 3% and the silicon content to 2% or less in order to obtain the graphitic distribution and pearlitic matrix structure which are characteristic of "high-test gray cast irons." Cast iron is essentially an alloy of iron and carbon, and the properties desired are obtained primarily by regulation of the silicon content. In making any alloy addition, attention must be given to the composition and properties of the base iron. Thus, the influence of any other element in the alloy will either modify or be modified by the carbon and silicon contents. In passing, it may be stated that high percentages of silicon render iron very hard, but resistant to corrosion, and therefore, such alloys find considerable use in the chemical industry.

TITANIUM. This element resembles carbon and silicon in its chemical properties, but its principal value lies in its powerful deoxidizing action on molten iron which tends to make castings made from it sound and homogeneous, and thus the physical properties are improved. Since about 1900, a number of American and German investigators have worked on the problem, and when the conditions of the experiments were maintained properly, the results agreed amazingly well. The research on the influence of titanium in cast iron which had been carried on to 1912, was excellently summarized by Stoughton[11] who appended to his paper a complete bibliography. The conclusions were that it is entirely possible by correct treatment to increase the strength of cast iron by from 30 to 50%, but the conditions under which the alloying material (usually 15% ferro-titanium) must be carefully regulated and maintained. In the discussion of Stoughton's paper it was stated that titanium reduces the chill of iron quite noticeably by virtue of its graphitizing effect. In car wheel work when titanium is used, the silicon and manganese contents must be adjusted in order to get the same depth of chill as in untreated metal. The chill is harder and tougher, however, and therefore desirable.

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[1] Everest, Bulletin No. 10, British Cast Iron Research Association, 4-6 (1925)

[2] Keep, Journal Franklin Institute, 126, 220 (1888). Transactions American Institute Mining Engineers, 18, (1889)

[3] Moldenke, Principles of Iron Founding. New York: McGraw-Hill, 64-6 (1917)

[4] Hogg, Journal of the Iron and Steel Institute. II, 104, (1894)

[5] Styffe, Journal of the Iron and Steel Institute. I, 584, (1894)

[6] Melland and Waldron, Journal of the Iron and Steel Institute, II, 244, (1900)

[7] Adamson, Journal of the Iron and Steel Institute, I, 75, (1906)

[8] Everest, Foundry Trade Journal, 36, 169 (1927)

[9] Irmann, Zeitschrift für Metallkunde, 18, 121-2 (1926)

[10] Piwowarsky, Stahl und Eisen, 45, 289-97 (1925)

[11] Stoughton, Bulletin American Institute Mining Engineers, 71, 1245-75 (1912)

Lamort[1] studied the titanium-iron alloys metallographically and concluded that they consist of solid solutions up to 6% titanium. The eutectic containing 13% titanium melts at 1300° C. He studied the structure of commercial ferro-titaniums and found considerable differences among them which accounts for the difficulties encountered in getting the desired results from adding titanium to cast iron.

According to Piwowarsky[2], titanium exerts an influence similar to that of silicon on the formation of graphite, but in a stronger degree. The maximum graphitization is attained by the addition of 0.1% titanium. Above this point the titanium ceases to influence the formation of graphite but improves the mechanical properties of the metal because of its cleansing effect. The resistance of cast iron to acid corrosion is increased by the addition of larger amounts of titanium. Bardenheuer and Zeyen[3] studied the influence of titanium primarily as a deoxidant and their experiments showed that when ferro-titanium is used for this purpose, the graphite content is increased with a consequent lowering of strength. In annealed chill castings the titanium was found to increase the elongation.

Hurst[4] has very recently reviewed the subject, and he emphasizes the fact that ladle additions of ferro-titanium are expensive and have held back development in this field. In addition to the high cost the ferro-titanium alloys have high melting points and are difficult to handle satisfactorily. Even apart from the consideration of cost, Hurst states that the most satisfactory way of making titanium additions is by the use of titanium-bearing pig irons which can now be obtained.

ZIRCONIUM. A patent was granted to Weiss[5] which covered the addition of 1% zirconium to molten iron in the form of fine metal, alloy, carbide, or silicide, in order to increase strength and toughness.

Moldenke[6] carried on experiments to determine the influence of zirconium on cast iron. He used an alloy containing 30.6% zirconium. Small percentages behaved well in melting and indicated a purifying action. The larger percentages chilled the metal and rendered it difficult to pour. In general, however, he found no appreciable improvement in the properties of the castings, especially when the iron was correctly melted.

Guertler[7] classes zirconium as a deoxidizer, but states that no great advantage accrues from its use.

Smalley[8] refers to Moldenke's work and goes on to state that he could detect no improvement from the introduction of zirconium in quantities up to 0.20% whether steel was melted with the iron or not, and whether charcoal or coke pig iron was used.

CERIUM. Cerium is one of the rare earth metals which is best known in the form of the iron alloy which is used as the so-called flint in cigar and gas lighters. It has not shown any great promise as an alloying element to be added to cast iron.

Moldenke[9] tried adding cerium, and its congener, lanthanum, to gray and chilling irons with various proportions of an alloy containing 70% of the rare metals. Tests on iron containing up to 0.15% indicated that the deoxidizing action was very marked, but the question as to whether any beneficial results other than greater machineability and soundness could be obtained, was left for further investigation.

Smalley[10] attempted to reproduce these results adding up to 0.10% of cerium by means of a 70% ferro-cerium alloy in stick form. No beneficial effects were noted up to 0.05%, but with 0.10% a slight strengthening effect was noted. There was no increase in fluidity or decrease in shrinkage. The indication was that the increased strength was due rather to the temperature than to the deoxidizing action of the cerium.

Spring[11] made two tests with gray cast iron and found that the addition of cerium reduced the sulphur content, increased both tensile and transverse strength and the deflection considerably.

Schwartz and Guiler[12] state that cerium and the other rare earth metals, when present in small amounts in iron of normal composition, interfere with graphitization.

THORIUM, TIN AND LEAD. No investigations of the influence of thorium or lead appear to have been reported. This is doubtless due to the rarity of thorium metal and its alloys on the one hand, and the volatility of the lead on the other.

Guertler[13] investigated the influence of tin on gray cast iron and found this element to increase the hardness and the latter was maintained at high temperatures.

Hamasumi[14] worked with tin in amounts up to 6% and showed that up to 2% it increases the strength and hardness slightly, but with over 2%, the irons become hard and brittle. Schwartz and Guiler[15] class tin among the metals which inhibit graphitization.

THE ELEMENTS OF GROUP V

PHOSPHORUS. This element is always present in cast iron, and its influence is well known. Actually, a discussion of this element does not belong in this paper.

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[1] Lamort, Ferrum, *11*, 225-37 (1914)

[2] Piwowarsky, Stahl und Eisen, *43*, 1491-4 (1923)

[3] Bardenheuer and Zeyen, Giesserei Zeitung, *15*, 1124-8 (1928)

[4] Hurst, Foundry Trade Journal, *41*, 173-4, 176 (1929)

[5] Weiss, United States Patent, 982,326 Jan. 24, 1911

[6] Moldenke, The Foundry, *48*, 878-9 (1920)

[7] Guertler, Giesserei Zeitung, *8*, 134-5 (1921)

[8] Smalley, Engineering, *114*, 277-80 (1922)

[9] Moldenke, Iron Age, *105*, 324-5 (1920)

[10] Smalley, Engineering *114*, 277-8 (1922)

[11] Spring, Trans. American Foundrymen's Association, *30*, 629-30 (1922)

[12] Schwartz and Guiler, Trans. American Foundrymen's Association V. 33, 639-45 (1925)

[13] Guertler, Giesserei Zeitung, *8*, 134-5 (1921)

[14] Hamasumi, Science Reports of Tohoku Imperial University *13*, 133-78 (1928)

[15] Schwartz and Guiler, Trans. American Foundrymen's Association, V. 33, 639-45 (1925)

It is sufficient to say that owing to the formation of iron phosphide and the phosphide eutectic which has a low melting point, the presence of phosphorus in molten cast iron increases its fluidity. Phosphorus appears to have little direct effect on the carbon, but it prolongs the cooling of melted iron, and thus allows more time for the separation of graphitic carbon. High phosphorus content leads to segregation and hard spots in castings. It is seldom used in amounts over 0.75% and for heavy castings it is kept as low as 0.10%.

VANADIUM. Vanadium is one of the lesser-known metals which have been proved to possess a powerful influence on steel. Obviously with the success attained by the vanadium steels, the element has been investigated in relation to its possible influence on the properties of gray cast iron. A rather considerable literature on this subject is available.

Moldenke[1] added up to 0.15% vanadium to various grades of cast iron, with and without the previous addition of manganese as a deoxidizer. In every case an increase of tensile strength was noted, being as great as 25% in the case of gray cast iron.

J. Kent Smith[2] explained the action of vanadium in improving the properties of cast iron by its great avidity for oxygen and nitrogen, and therefore held that its value lay first in its cleansing power, and second[3] by its solid solution in the carbonless constituent of the iron, rendering the molecules of its constituents more coherent than ever, and their crystals more resistant to abrasion, wear, and less susceptible to breakage or disintegration along their cleavage lines. Vanadium also tends to prevent graphitization. Norris[4] stated that up to 0.2% the strength of the iron increases 10-25% because of a more uniform distribution of graphite and the consequent finer grain. The results of very successful tests on locomotive cylinders made of vanadium cast iron indicated that the wear resistance is much higher than that of ordinary cast iron.

Hatfield[5] carried on a rather extensive investigation on vanadized cast iron and came to the conclusion that vanadium additions have a slight but definite beneficial influence on the physical properties, but disagreed rather violently with Smith as to the explanation. Hatfield holds the view that there is no need for scavenging action in properly melted cast iron, and that the value of the vanadium is due to its influence in "preserving the carbon in the combined state."

Fitch[6] experimented with pig iron containing vanadium and titanium, but since he was primarily interested in the effect of varying percentages of scrap in the mixture, his results do not indicate any particular advantage due to the presence of the vanadium.

Campion[7] reviewed the work of previous investigations, but presented no new data.

Smalley[8] using a 35% ferro-vanadium added vanadium to molten cast iron in quantities up to 0.1%. His results confirm Moldenke's statement that small quantities of vanadium improve the strength of the iron. The hardening effect of Hatfield was not observed which "suggests that Hatfield's results are more than probably accounted for by either a variation in the casting temperature or the initial temperature of the mold, factors which he does not appear to have taken into account."

Smith[9] sums up his earlier work and states that vanadium has a beneficial influence when used up to 0.20%. Dirty, burnt irons treated with vanadium are cleansed of their oxygen content and the increase in strength is quite appreciable. The increase is less when clean cylinder iron is treated with vanadium, although the latter undoubtedly has a beneficial influence.

Donaldson[10] states that the addition of 0.125% vanadium produced a slight increase in transverse strength and also in hardness.

The most recent contribution to the literature of vanadium-treated cast iron is by Hurst[11], in which it is stated that vanadium exercises a strong influence on the grain, causing a more even distribution of the graphite. In chilled castings, vanadium produces a deeper and stronger chill. Vanadium cast iron has proved most satisfactory in locomotive cylinders from the standpoint of wear, and in glass-bottle molds, in which the high degree of polish attainable decreases the tendency toward sticking.

The general inference to be drawn from the results of these investigations is that vanadium has a small beneficial effect on cast iron, due perhaps more to its avidity for oxygen and nitrogen, than to any real alloying effect.

THE ELEMENTS OF GROUP VI

SULPHUR, SELENIUM and *TELLURIUM.* Oxygen, sulphur, selenium and tellurium are related chemically, the similarity between the last three being quite marked. The effect of sulphur on cast iron is common knowledge and its discussion has no place in this paper. It may be stated that sulphur is one of the few elements present in cast iron which does not oxidize out and consequently its content increases with repeated melting. It tends to make the iron hard and brittle because it inhibits graphitization. Molten iron containing a high sulphur content is sluggish and sets quickly giving rise to unsound castings. The detrimental effects of sulphur may be largely controlled and certainly lessened by insuring the presence in the mixture of sufficient manganese.

There is apparently no record of any work having been done with selenium and tellurium which are however relatively expensive. It is quite probable that small amounts of each element exist normally in the pig iron having entered it from the ore and fuel, since both are widely distributed in nature. In any case, the probability is that these elements would show an influence analagous to that of sulphur.

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[1] Moldenke, Iron Age, *81*, 522-4 (1908)

[2] Smith, The Foundry, *33*, 268-70 (1909)

[3] Hatfield, Journal of the Iron and Steel Institute, *83*, 318-31 (1911)

[4] Norris, Chemical and Metallurgical Engineering, *9*, 361-3 (1911) Trans. American Foundrymen's Association 479-88 (1911);

[5] Hatfield, Journal of the Iron and Steel Institute, *83*, 318-31 (1911)

[6] Fitch, The Foundry, *43*, 179-181 (1915)

[7] Campion, Foundry Trade Journal, *20*, 467-70 (1918)

[8] Smalley, Engineering, *114*, 279-80 (1926)

[9] Smith, Foundry Trade Journal, *28*, 52-53 (1923)

[10] Donaldson, Foundry Trade Journal *32*, 553-6 (1925)

[11] Hurst, Foundry Trade Journal *41*, 173-4, 176 (1929)

OXYGEN. This element has been considered detrimental to cast iron from the earliest times but in 1914, Johnson[1] published the results of his extensive research in the mechanical properties of pig and cast iron. He claimed the presence of oxide of iron in charcoal pig iron was responsible for its superior mechanical properties as compared with coke pig iron. He found that charcoal iron containing 0.04% to 0.10% oxygen had exceedingly good mechanical properties as compared with the more normal properties of coke iron containing 0.015 to 0.025% oxygen. It was also demonstrated that by melting ordinary pig iron with spongy, highly-oxidized iron it was possible to obtain a much stronger product. Deoxidization of the stronger iron reduced the strength to more extent. The improvement in the quality was ascribed to the presence of the oxide of iron causing the graphite to separate in nodular form, instead of in plates or flakes as is common in the weaker irons.

This communication set in motion a controversy in which the latest word was spoken by Oberhoffer and Piwowarsky[2] in 1927, when they published the results of a very careful investigation of twenty coke pig irons and fourteen charcoal irons and failed to establish any connection between manufacturing conditions and the oxygen present in the iron. In thirty cast irons they found the amount of oxygen higher than in the pig irons and that 0.045% appeared to be the upper permissible limit. Johnson considered the oxygen to be combined with iron, but by more accurate methods of determination Oberhoffer and Piwowarsky have demonstrated that the oxygen is present principally in combination with the silicon. It is probable that the extreme difficulty of determining oxygen in iron has been largely responsible for the differences in the results of the various investigations and to these is due the controversial aspect of the problem. The situation has been well summed up in The Metallurgist, 3, 101-2 (1927) and by Moldenke[3] in connection with a discussion of the work of Oberhoffer and Piwowarsky. The general outcome of the matter seems to indicate that irons melted with a high blast and consequently tapped at a higher temperature than normal are better in quality although the oxygen content is not increased.

Chromium, molybdenum, tungsten and uranium are members of Group VI and they show a marked resemblance to each other. In the form of ferro-alloys they have been added to cast iron and their influence observed. Chromium is probably the most important alloying element, with the exception of nickel, now in use, as the result of years of scientific investigation. The general subject is so large and so familiar to the foundrymen, that its discussion is not considered as being within the scope of this paper. It should be sufficient to quote Donaldson[4] who states that "It appears to be definitely established that 0.5% chromium in the presence of 1 to 2% silicon increases the tensile and transverse strength and hardness of cast iron. This increase in strength is brought about by the chromium preventing the formation of graphite and producing a more stable double carbide of iron and chromium, which crystallizes out with the pearlite." Chromium also has a definite application in the field of heat-resisting irons, because chromium irons show little growth under conditions of repeated heating and cooling.

MOLYBDENUM. According to Donaldson[5], Campion was the first investigator to study the influence of molybdenum in cast iron. He found that 1% increased the strength and decreased the hardness. Smalley[6] found that 0.1% molybdenum closed the grain of gray cast iron without appreciably affecting the hardness. The addition of 0.15% molybdenum to an ordinary gray iron containing 2% silicon, reduces the tensile and compression strengths and the chilling power, exerted little effect on the hardness and increased the transverse strength and deflection. The presence of 0.5% molybdenum, reduced slightly the chilling power, but improved the other properties, especially the compressive and transverse strengths. On cylinder iron the addition of 1.5% molybdenum had the effect of increasing the strength materially. On common gray iron 1.5% molybdenum brought about a general improvement although to a lesser extent. Molybdenum has a tendency to prevent graphitization but the formation of mixed crystals with the iron is the reason for the improvement of properties. When over 0.5% molybdenum is added to the cast iron, the machineability is decreased. Piwowarsky[7] was able to substantiate Smalley's results with iron containing up to 0.5% molybdenum, but found that with an increase to 1% there was no corresponding improvement in properties. This investigation states that molybdenum and tungsten influence the cast iron more favorably than any other metals on account of their tendency to form mixed crystals.

TUNGSTEN. In a report on the progress of the iron and steel industry made in 1874[8] the statement is made that "the presence of a certain percentage of the metal tungsten is now fully admitted to modify considerably the properties of both cast iron as well as steel, its addition being claimed as an improvement by its rendering the metal at the same time harder, more compact, and tougher with a finer grain in the fracture." Tungsten-alloyed cast iron was then in use in Germany in hard rolls, pinions and for other castings in which great hardness is desirable. Up to 4% tungsten was added.

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[1] Johnson, Bulletin of American Institute of Mining Engineers *85*, 1-40 (1914)

[2] Oberhoffer and Piwowarsky, Giesserei Zeitung, *14*, 197-202 (1927)

[3] Moldenke, Iron Age, *120*, 75-6 (1927)

[4] Donaldson, Foundry Trade Journal, *32*, 553-6 (1925)

[5] Donaldson, Foundry Trade Journal *32*, 553-6 (1925)

[6] Smalley, Foundry Trade Journal *27*, 3-5 (1923)

[7] Piwowarsky, Stahl und Eisen *45*, 289-97 (1925); Foundry Trade Journal *31*, 331-4, 345-6 (1925)

[8] Forbes, Journal of the Iron and Steel Institute, *8*, 470-1 (1874)

Donaldson[1] states that Campion found that 1% tungsten increased the strength of cast iron, but reduced the hardness, and that a 1.5% addition to an ordinary gray cast iron increased the tensile strength 51.5% and that in another sample containing 1.28% tungsten, the tensile strength was increased 55.2%.

Piwowarsky's experiments[2] indicated that 0.5% tungsten influenced favorably the mechanical properties of cast iron. In addition to increasing the tensile, transverse, and compressive strengths there is also an increase in impact resistance. The tungsten promotes a feeble graphitization, again the improvement being due to the formation of mixed crystals of iron and tungsten giving use to a new constituent, tungsten-ferrite.

Donaldson[3] states that the addition of 0.5% tungsten brings about increased strength at 400° C., after prolonged annealing. The growth of this alloy under repeated heating and cooling is practically nil.

URANIUM. Smalley[4] seems to have been the first investigator to determine the influence of uranium on cast iron. He found that in quantities under 0.20% uranium had no effect on the fluidity, shrinkage, tensile, and transverse strength of ordinary gray cast iron.

Foote[5] added uranium in the form of ferro-uranium to ordinary gray cast iron of low silicon content in quantities up to 0.50%. The results indicate that up to 0.2% addition there is an improvement in transverse and tensile strength, but beyond that there is no appreciable advantage. The uranium has a tendency to cause a finer separation of graphite which results in a close grained, homogeneous metal.

THE ELEMENTS OF GROUP VII

MANGANESE. The seventh group includes the halogens, fluorine, chlorine, bromine, and iodine all of which are non-metallic, and because of their properties have no significance in connection with the study of alloy-cast iron. Manganese is the only metal in the group, and its importance in relation to cast iron is known to all foundrymen. As stated earlier in this paper, cast iron always contains some manganese which is derived from the original iron ore. Manganese has two major effects in cast iron. It tends to stabilize the iron carbide or cementite, and it reacts with sulphur to form manganese sulphide which is less harmful to the casting than iron sulphide. In general manganese strengthens and hardens the iron, and increases the shrinkage. The discussion of the effect of naturally-occurring elements is without the scope of this paper, but it may be stated that much investigational work has been carried out, and a very comprehensive literature of the subject is available.

THE ELEMENTS OF GROUP VIII

The elements of this group form a transition from the acidic elements of the sixth and seventh groups to the basic elements of the first and second. It is therefore necessary to place them in an eighth group although this appears to violate the theory of octaves, namely, that the properties of every eighth element, when they are arranged in the order of their atomic weights, are similar.

NICKEL. Iron itself is a member of this group. Nickel and cobalt which are closely related to it chemically have been found to have most important influences on the properties of gray cast iron containing them. Nickel and cobalt behave in much the same way, and since nickel is the more plentiful and cheaper it has found its way into modern foundry practice to a greater extent than any other alloying material. The International Nickel Company has sponsored fundamental research in both this country and England, and much time has been given to working out the details of the practical application of nickel to cast iron. The result is that a very large literature has been built up, and the subject is so broad that it would require a separate paper for its discussion. Nickel-cast iron is now regularly manufactured and its success is another evidence of the value of concentrated scientific research.

It has been found that the addition of 0.5 to 1.0% nickel improves the properties of gray cast iron by 20 to 30%. With a higher content up to 2%, because of its graphitizing power, the strength becomes less. The improvement in the properties of cast iron by the addition of nickel is attributed to the formation of mixed crystals. An addition of 3% nickel to ordinary medium-silicon gray cast iron renders the grain very fine, and although there is much graphite present it is so fine that the strength is not decreased. The machineability is most satisfactory.

CONCLUSION

The effect of the presence of various elements on the properties of cast iron has been discussed briefly in the light of the available literature on the subject. It will be noted that certain elements occur naturally in cast irons, and that the addition in relatively small amounts of other less widely known elements may affect the properties of the alloyed iron very favorably. The alloying elements appear to fall into two classes, those whose value depends upon the formation of actual compounds or solid solutions with the iron (the true alloys), and those which have great affinity for oxygen and sulphur, which improve the properties of the iron by virtue of the purification which they bring about. Some of the elements, as for instance, vanadium, react in both ways.

The field of alloy cast irons is so vast that in spite of the amount of work which has already been carried out, the possibility of improving the quality of cast iron by this method is still unlimited. By attacking the problem from the point of view of the Periodic System an effort has been made to set forth the existing information in the most orderly manner possible. It is hoped that this paper will stimulate further thought on the part of the foundrymen and be of help in indicating the way for further investigation.

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[1] Donaldson, Foundry Trade Journal, 32, 553-6 (1925)
[2] Piwowarsky, Stahl und Eisen, 45, 289-97 (1925)
[3] Donaldson, Foundry Trade Journal, 31, 517-22 (1925)
[4] Smalley, The Foundry Trade Journal, 27, 3-5 (1923)
[5] Foote, The Foundry, 52, 105-6 (1924)

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